PERFORMANCE OF n-TiO_2/dye/p-CuI INCORPORATED WITH NEW CHELATING AGENT FOR SOLID STATE DYE SENSITIZED SOLAR CELL APPLICATIONS

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Abstract

A new approach to produce CuI-related composite film for dye-sensitized solar cell applications is demonstrated. This paper introduced an alternative organic chelating agent, called tetramethylethylenediamine (TMED@TMEDA), to be used as CuI crystal growth inhibitor and as an alternative to the previously used chelating agents in the fabrication of DSSCs. Investigation was conducted on the use of the proposed chelating agent in conjunction with eco-friendly p-type materials in the preparation of dye-sensitized solar cells. It is found that highly (111) oriented CuI film with improved quality could be easily prepared on FTO glass substrate using TMED. Furthermore, the TMED-chelate CuI film exhibit improved band-gap photoluminescence, indicating that TMED is a kind of reagent in inorganic synthesis that is more effective than using either 1-methyl-3-ethylimidazolium thiocyanate (MEISCN) or triethylamine hydrothiocyanate (THT). So far, the use of TMED in CuI solution in the fabricating of solid-state DSSC has not yet been reported. Subsequently, an n-TiO_2/dye/p-CuI solid-state DSSC cell was fabricated and characterized. The chelating agent or ligand that was introduced not only controls the CuI crystal growth and acts as a protective coating for CuI nanocrystals but improves the electrical contact between Titanium dioxide (TiO_2) particles thus improving the cell performance. Current-voltage characteristics highlighted a larger conversion efficiency of fabricated samples.

Introduction

Attempts have been made to convert electrolyte-based DSSC cells to solid-state DSSC cells and p-type semiconducting materials such as spiro-OMeTAD and copper (I) iodide (CuI) have been tested as hole conductor for the cells [1-2]. Also, studies were conducted to improve the performance of the solid-state DSSCs as the device has been reported to deliver small photocurrents and are found to be unstable. However, one major restriction in the fabrication of DSSCs is to fill the pores of an n-type semiconductor TiO_2 film with a p-type semiconductor in order to establish firm and stable contacts with the dyed surface. The crucial problem that needs studying is related to the contact between dye monolayer and holes conductor as the n-type TiO_2 pores could only be partially filled with the p-type material, particularly when using thicker films [3].

To date, one well-known approach that most researchers was to employ in the fabrication of DSSC is to use CuI as holes conductor probably because it is not water-soluble, however, CuI is soluble in acetonitrile at room temperature. Its solubility in acetonitrile is attributed to the formation of weak CuI-acetonitrile adducts whose coordination originates from a significant π bank-bonding from cuprous ion to nitrogen, as confirmed by infrared and Raman spectra investigations [4-5]. The formed CuI-acetonitrile adducts are metastable and can easily revert to CuI materials with a ligand missing, but the CuI deposited from acetonitrile solution usually consists of large cubic crystallites resulting in a film with a rough surface. Such a structure cannot form stable and firm contact with other functional materials, hence limiting its application in many optoelectronic devices [6]. Besides, CuI films prepared by evaporating the solution when exposed to light will emit radiation with higher energy than CuI band-gap causing CuI to photo-decompose and iodine is liberated; this photo-decomposition will strongly affect the stability of optical and electronic properties of the film. One example of this emission is when there is variation in the amount of iodine adsorbed on the surface the CuI film resulting in instability of the film.

Tennakone et al. has formulated and synthesized CuI thin film using 1-methyl-3-ethyl-imidazolium thiocyanate (MEISCN) by incorporating ligand for DSSC [7-8], but MEISCN is rather costly to produce as the separation process during its purification involves a rigid chemical procedure. However, a more effective ligand, called triethylamine hydrothiocyanate (THT) has been identified that could be used in the fabrication of CuI for application in DSSC cells [9-10] with efficiency of approximately 3.8 %. In both cases, the function of the ligand is to suppress the expansion of CuI particles as it is able to inhibit the growth of CuI crystal size and to fill the pores of the nanocrystalline n-TiO_2 semiconductor [3].

In this paper, a novel approach to produce a new CuI-related composite film is introduced where an alternative organic chelating agent, called tetramethylethylenediamine (TMED@TMEDA), to be used as CuI crystal growth inhibitor. Subsequently an n-TiO_2/dye/p-CuI solid-state DSSC cell was fabricated and characterized. Highly efficient solid-state DSSC (TiO_2/dye/CuI) with improved efficiency was fabricated by controlling the pore- filling of the dyed porous TiO_2 layer with chelating agent capped nanosized CuI crystals. The chelating agent or ligand that was introduced not only controls the CuI crystal growth and acts as a protective coating for CuI nanocrystals but improves the electrical contact between TiO_2 particles thus improving the cell performance. The electrical characteristic of the cells shows a very good electrical rectification and photovoltaic efficiency. This shows that the performance of solid-state solar cells is very much dependent on the role of p-type materials pore-filling into TiO_2. So far, the use of TMED in CuI solution in the fabricating of solid-state DSSC has not yet been reported.

Experimental procedure

All the chemicals used in this research were as obtained from the suppliers and no further purification was carried out. TiO_2 films of approximately 15 μm thick were prepared using squeegee technique and Figure 1 shows the flow diagram of the process involved in the preparation and deposition of the TiO_2 thin film.

After the TiO_2 films have been prepared, the films are soaked for 24 hours in Rhodamine B dye. The preparation and deposition procedure of CuI thin films and TMED-chelate CuI thin films onto dye/TiO_2/FTO glass substrates is done using a technique of drop and leave for a while then spin coated. Figure 6.2 shows the flow diagram of the process involved in the preparation and deposition of the CuI thin film.

Results and Discussion

1 *Structural Properties*

In this study, the morphology of the deposited films produced after each process was investigated, including that of the TiO_2 film, and this is shown in Figure 3. In Figure 3(A), shows the morphology of TiO_2 using squeegee method; it is observed that large pores are formed on the surface of the film and the pores are assumed to also exist inside the film. Theoretically, when these pores are filled with p-type materials, the contact between the dye and p-type materials would be improved [11-12]. The deposition method employed produces films with a rough surface and the roughness of the surface influences the amount of light that is absorbed, hence affecting the efficiency of energy conversion [13]. The pores and surface roughness of TiO_2 films produces here is very much dependent on the volume of polyethylene glycol (PEG) and triton X used, and an appropriate amount of both materials is necessary to prevent the formation of heavy cracks.

The morphology of CuI film prepared without the addition of TMED is presented in Figure 3(B), and large CuI crystals are observed scattered on the deposited film indicating that the crystallization process happened very fast and is uncontrolled [3]. However, the CuI films morphology prepared with the addition of TMED, as shown in Figure 3(C), shows significant reduction in the CuI particles compared to that prepared without the use of TMED showing that TMED can control the crystallization of CuI by acting as a surfactant. From the result, the smaller CuI crystals can better fill the TiO_2 pores, hence improving the contact with the dye monolayer. Another phenomenon observed in Figure 3(C) is a fine layer covering the CuI crystal surface; the layer serves to reduce immediate contact between the unexposed dyed TiO_2 particles to the CuI crystals, thus reducing the probability of short-circuiting between them. Also, this layer helps decrease degeneration of the CuI due to aging, hence increasing the lifetime of the solar cell [3]. Figure 3(D) shows the morphology of the CuI thin film with the addition of TMED deposited on dye/TiO_2/FTO substrate. The film is a very thin layer and its surface difference can be seen compared to the TiO_2 only film shown in Figure 3(A) because the reduced CuI crystals size has penetrated deeper into the TiO_2 film, other than covering the surface of the film.

One reason for the phenomenon is that the smaller CuI crystals penetrated the pores in the TiO_2 film gradually from surface down into the film, and finally cover the top of the film. Since the adsorption of TMED in CuI film results in smaller crystals, its average size is determined by the monolayer covering the film. Again, the optimum TMED concentration required was found to be the same order of magnitude as the amount of TMED needed for monolayer coverage of μm CuI crystallites. TMED being a ligand, its residue, formed at the grain boundaries after evaporation of the solvent, spread into a thin film around the surfaces.

EDX has been performed to verify that the film is composed only of TiO_2 and CuI, and this found to be so as can be seen in spectrum 1 and spectrum 2 shown in Figures 4. The EDX revealed that the composite film has only TiO_2 and CuI except that carbon dioxide is also detected which could be from the unresolved TMED element when the film is annealed or due to contamination from the surrounding environment. Furthermore, since the CuI film is prepared from saturated solutions, all the particles will not be completely reduced. The particles that underwent incomplete process as growth inhibitor will be left on top of the film as can see in the area of spectrum 1 while the completely reduced particles will gradually penetrate into the pores of TiO_2 as in spectrum 2.

Figure 5 shows the EDX measurement, simultaneously represents the SEM images, and of the cross-section of the fabricated films and it is observed that pore-filling in the TMED-chelate CuI thin films is more advanced. The large opaque areas found in cross-sectional SEM images of the TiO_2 layer signify good pore-filling in those areas, and the EDX measurements proved the covered area is a composite of TiO_2 and CuI film. Other elements that appear in the spectrum, like indium (In), are because the cross-sectional images was taken after the metal contact is deposited on top of the films. Elements like carbon dioxide and aluminum (Al) originate from unresolved TMED element after undergoing the annealing process or are contaminants from the surrounding environment.

Figure 6 shows X-ray diffraction spectra (XRD) for the TiO_2 film, TMED-chelate CuI film, TiO_2/dye/CuI (TMED) composite film and FTO substrate. The peaks noted in the TiO_2 film spectra can be assigned to the TiO_2 anatase structure and the peaks noted in the TMED-chelate CuI film spectra can be assigned to the CuI polycrystalline γ-phase structure. In the case of TiO_2/dye/CuI film spectra, other than the TiO_2 peaks, CuI peaks are also observed. A very strong TiO_2 (101) and TMED-chelate CuI (111) peaks at 2θ value around 25.5^{o} can be seen in the composite film proving that it is TiO_2/dye/CuI film.

2 *Electrical Properties*

The Current-Voltage (I-V) characteristics of the fabricated cells were examined using two-probe solar simulator (BUNKOH KEIKI-CEP2000) where all procedure and measurements are performed under room temperature. An array of indium (In) spots, each 1-mm in diameter, was evaporated on top of composite film as metal contact as shown in Figure 7. Also shown in the figure is the incident light, maintained at AM1.5 ($100 mW/cm^2$) that illuminated the p-type material during the measurement.

Figure 8 is the investigated photovoltaic performance of TiO_2/dye/CuI cell prepared without TMED. The characteristic values of the cell are $V_{oc} = 0.076V$, $I_{sc} = 0.026\ mA/cm^2$, a fill factor FF = 0.178 so that the resulting energy conversion efficiency is $3.54\ x10^{-4}$ %. For comparison purposes, the performance of TiO_2/dye/CuI (TMED) solid-state device DSSC are conducted, and is shown in Figure 9. The characteristic values for Sample A are as follows: $V_{oc} = 0.536V$, $I_{sc} = 10.12 mA/cm^2$, a fill factor FF = 0.7156, and the resulting conversion efficiency of the cell is 3.88%.

All the devices under study were annealed at $80^{o}C$ of temperature. In the case of CuI films without TMED, it is suggested that the CuI crystals large size results in poor electrical contact between the TiO_2 porous surface and the CuI crystal, and improper filling of the pores. The very poor electrical contact decreases the transfer of holes from the dye molecules to the CuI crystal. The uneven pore-filling of the films' void causes a lack in holes transportation in the CuI layer thus decreasing the overall efficiency of the solid-state DSSC [8].

In the case of CuI films with TMED, the CuI crystals small size together with an almost complete absence of voids in the CuI layer permits good contact between the dyed TiO_2 porous surface and the CuI crystals. Thus, as indicated by the increase in the short-circuit current, the device performance is affected by the pore-filling of the TiO_2 by the p-CuI (TMED) crystals together with the effect of heat energy from the annealing process. From the results, it is noted that there is an increase in short-circuit current in sample with the use of TMED. This increase indicates an intensification of the charge carriers mobility which create strong electric field inside the cell and is further supported by the complete filling of the pores between the nanoparticles by the transparent holes conductor [8].

Conclusions and summary

This research has demonstrated the operation of CuI solution without and with the incorporation of TMED using the drop and spin coating technique to deposit the films onto dye/TiO_2/FTO substrate, while squeegee method was applied to fabricate the TiO_2 films. Rhodamine B is used as dye in the cells for the purpose of absorbing photon. Indium was evaporated on top of the films in order to characterise the cell's electrical properties. In conclusion, highly efficient solid-state DSSC (TiO_2/dye/CuI) with improved efficiency was fabricated by controlling the pore-filling of the dyed porous TiO_2 layer with chelating agent capped nanosized CuI crystals. The chelating agent controls the CuI crystal size and protects the CuI crystals from degeneration. Looking at the electrical characteristics of the cells, a very good electrical rectification and photovoltaic efficiency is noted and this shows that the performance of solid-state solar cells is very much dependent on the role of p-type materials pore-filling into TiO_2. With incomplete pore-filling, the cell's resistivity is increased causing the degradation of current densities and resulting in poor energy conversion efficiency of the cell under sunlight.

This paper has shown that TMED-chelate CuI film is a very promising new holes-conductor that can be implemented in solid-state DSSC as it produces relatively high energy conversion efficiency, and it is found photocurrent can be increased with the use of thicker TiO_2 film. The dye used in this study is not necessarily the best absorber to be implemented in solid-state DSSC but the results show that, when interfaced with TiO_2/dye/CuI, Rhodamine B can produce significant photocurrents.

However, optimization of the various stages of the CuI film's fabrication have yet to be conducted which include parameters such as reproducibility and stability of the cell. An efficient deposition technique should be improved to produce better penetration and distribution of the p-type materials into the TiO_2 pores. Although good penetration and pore-filling is observed, while high energy conversion efficiency has been achieved, there is still room for further improvement in pore-filling, especially down at the lower levels of TiO_2 film. Also, other factors such as electrical contact between the dye and hole conductor, and filling of the TiO_2 pores by p-type materials need further investigation as it gives significant influence on the performance of DSSC cells. As for future work, studies should be carried out to find new techniques that can facilitate more efficient and better distribution of CuI crystals to improve the energy conversion efficiency of DSSC cells.

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Mix 4.0g TiO_2 powder (P25, Aerosil Japan) + 0.5ml acetyl acetone

Stir in 2ml of pure water for 5 minutes; stir in additional 3ml of pure water for another 5minutes

Blend the mixed materials using mortar for 20 minutes.

Add 0.4g polyethylene glycol (PEG) and blend for 5 minutes

Add 2.5ml Triton X and continue blend for 5 minutes

Blended material ready for deposition using Squeegee technique

Heat and anneal deposited thin films at 100°C for 30 minutes; repeat process at 400°C

Figure 1: Preparation and deposition process flow of TiO_2 thin films.

1. Solution preparation (without TMED)
Precursor: Copper (I) Iodide
Solvent: Acetonitrile

1. Solution preparation (with TMED)
Precursor: Copper (I) Iodide
Solvent: Acetonitrile
Chelating agent: Tetramethylethylenediamine (TMED)

1. Stirring the solution
Stirring speed: 2.5 (scale); Stirring time: 3 hours

3. Deposition onto dye/TiO_2/FTO substrate
Method: drop a few drips and let it dry in ambient temperature for 5 minutes, then spin coating.
Instrument speed: 500 rpm
Deposition time: 20 minutes

4. Drying
Place in ambient temperature for 5 minutes

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5. Annealing using thermal furnace
Temperature: 80°C; Annealing Time: 10 minutes

Figure 2: Preparation and deposition process flow of CuI thin films

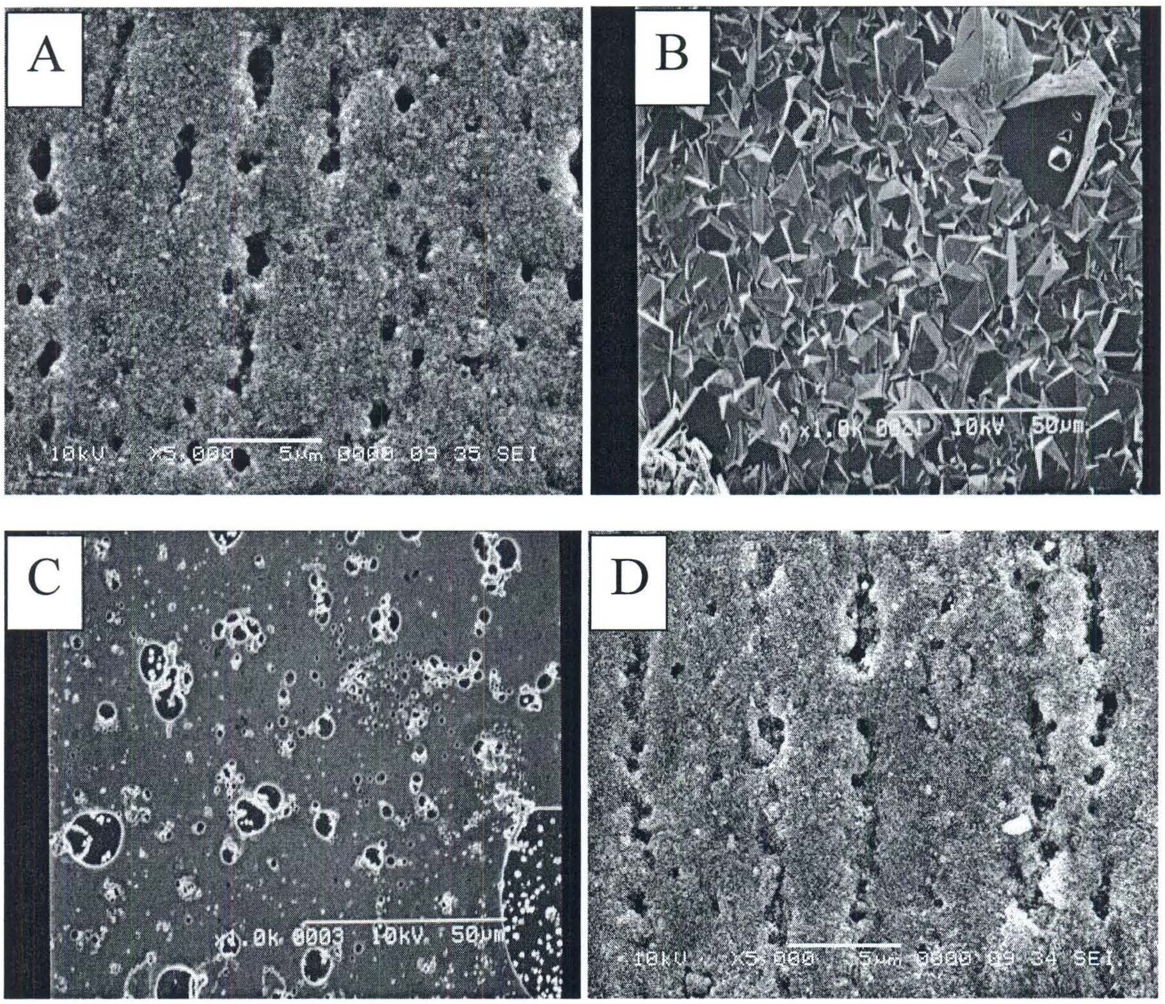

Figure 3: The morphology of each deposited films; (A) TiO_2 film, (B) CuI film without TMED, (C) CuI film with TMED, (D) TiO_2/dye/CuI (TMED).

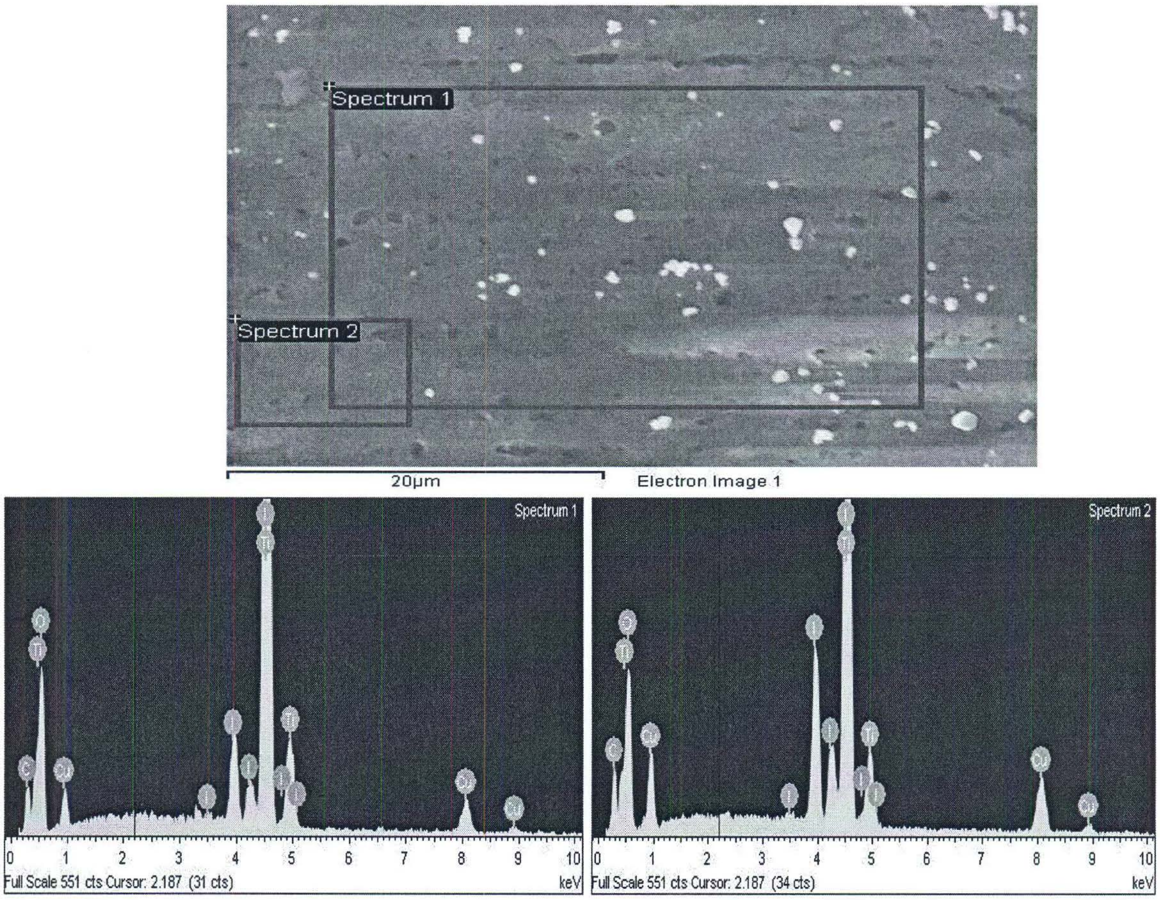

Figure 4: EDX measurements on top of TiO_2/dye/CuI(TMED) film surface.

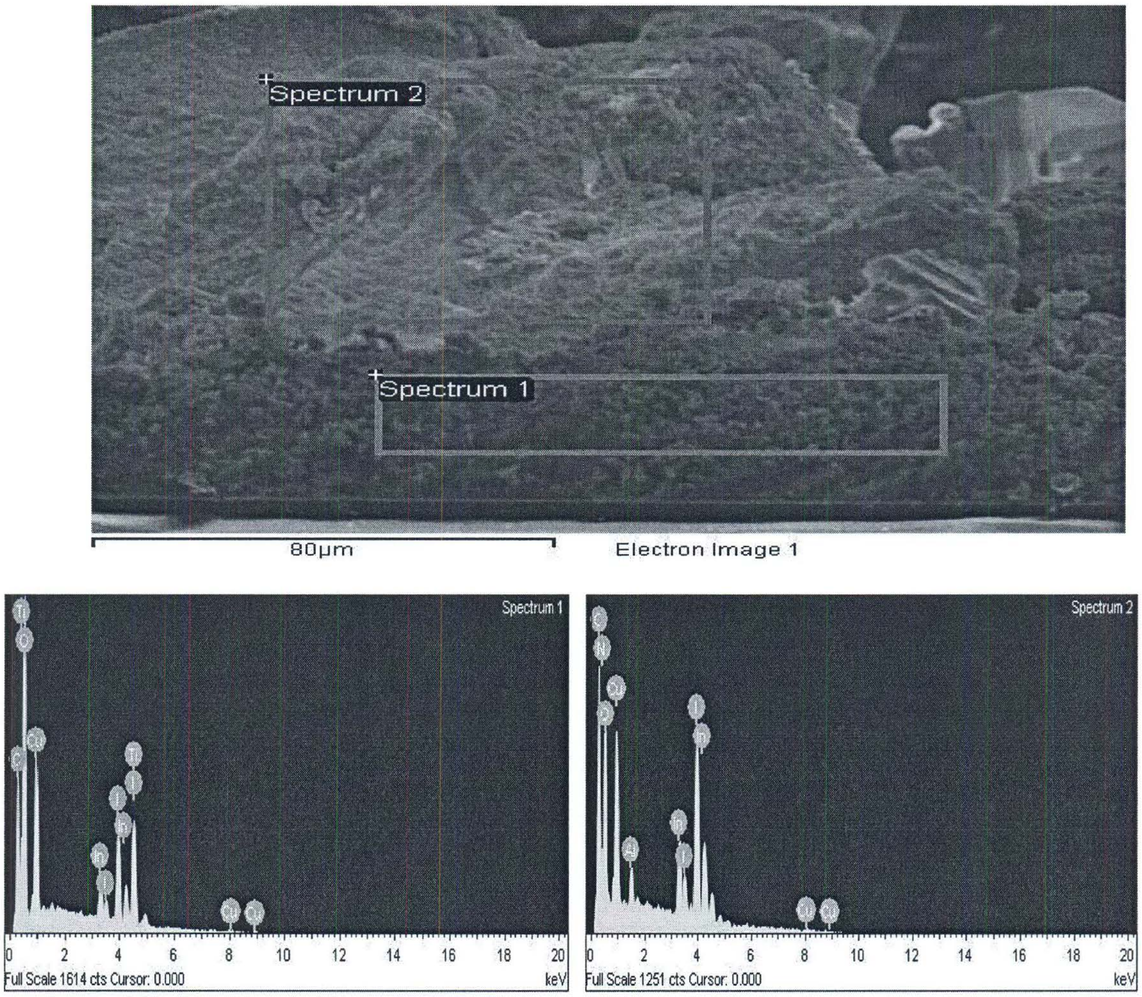

Figure 5: EDX measurement on the cross-section of TiO_2/dye/CuI (TMED) film.

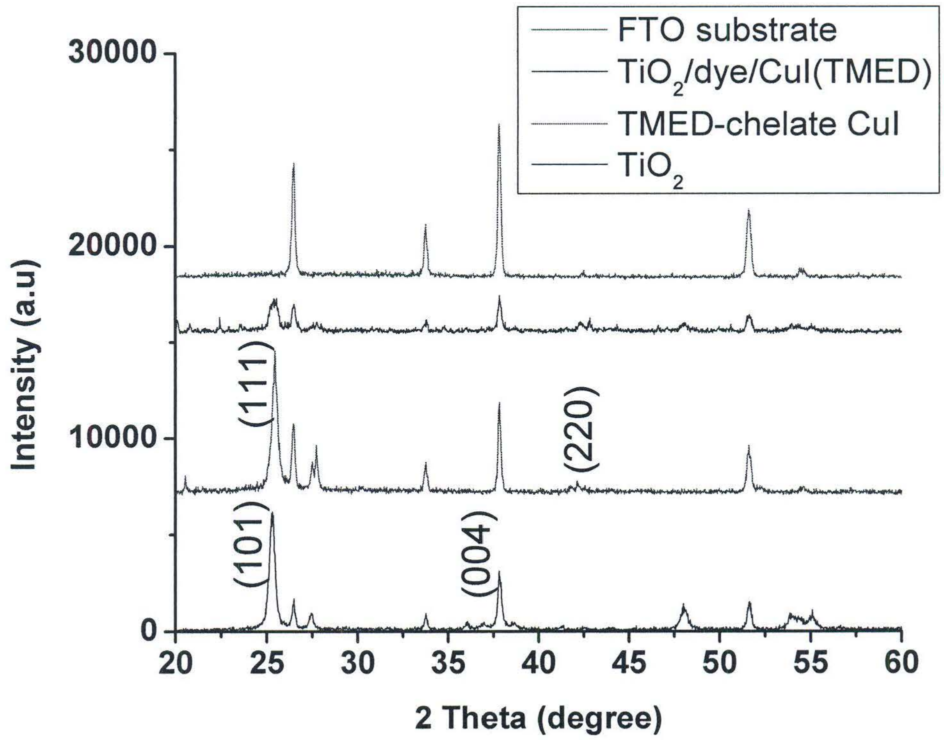

Figure 6: X-ray diffraction (XRD) spectra of the FTO substrate, TiO_2/dye/CuI (TMED) film, TMED-chelate CuI film, and TiO_2 film.

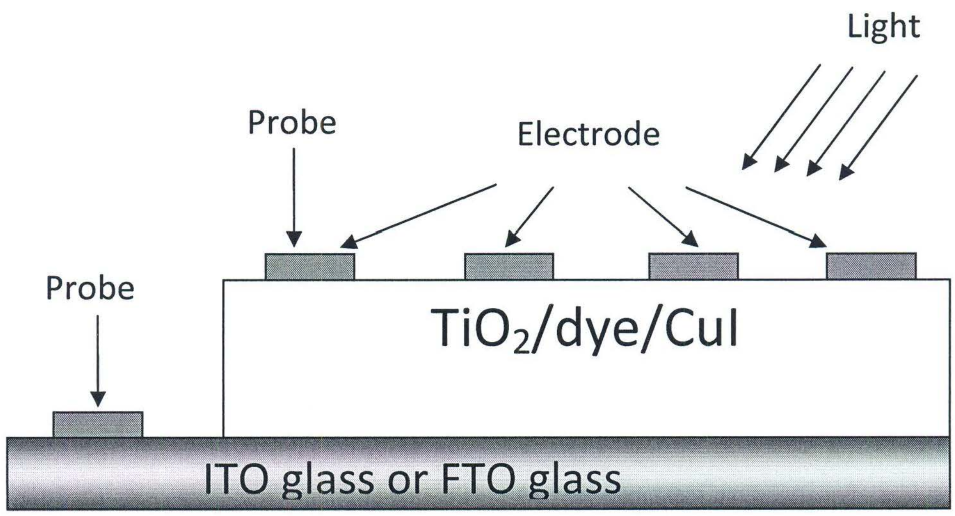

Figure 7: An array of electrodes for the I-V measurement.

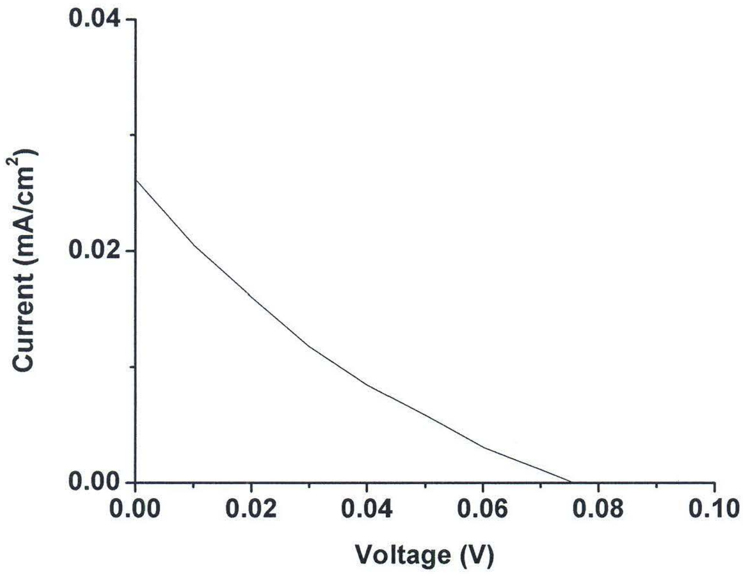

Figure 8: I-V characteristic of TiO_2/dye/CuI film without TMED.

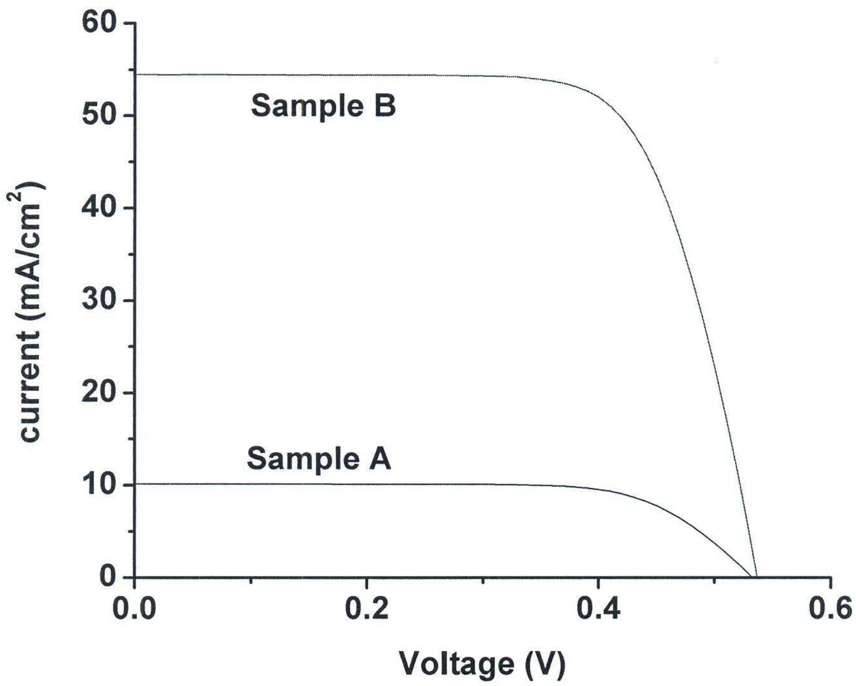

Figure 9: I-V characteristic of TiO_2/dye/CuI film with TMED